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(54) A PROCESS FOR THE PRODUCTION OF FOAM RESINS

(71) We, BAYER AKTIENGESSELL-
 SCHAFT (formerly known as Farbenfabriken
 Bayer Aktiengesellschaft), a body corporate
 organised under the laws of Germany of 509
 Leverkusen, Germany, do hereby declare the
 invention, for which we pray that a patent
 may be granted to us, and the method by
 which it is to be performed, to be particularly
 described in and by the following statement:—

This invention relates to a process for the
 production of a foam resin.

Polyurethane foam resins with a dense outer
 skin and a cellular core which are obtained
 by foaming in a mould (German Auslege-
 schrift No. 1,196,864 and French Patent Speci-
 fication No. 1,559,325) are eminently suitable
 for the mass production of lightweight con-
 structions, e.g. for the furniture, vehicle and
 building industries.

The moulded polyurethane products are
 produced from a foamable reaction mixture
 which consists of polyisocyanates, compounds
 which contain at least two hydrogen atoms
 capable of reacting with isocyanates, and addi-
 tives. Such a foamable reaction mixture is
 introduced into a closed mould which is
 capable of being kept at an elevated tempera-
 ture. The reaction mixture foams up inside
 the mould and solidifies in a highly compressed
 state. The synthetic resin completely fills the
 mould and exactly reproduces the internal
 surfaces of the mould.

The moulds are preferably made of a
 material which has a very high thermal
 capacity and thermal conductivity, preferably
 metal, but other materials, such as synthetic
 resins, glass and wood, may also be used.

The mould is provided with a mould-
 parting agent to prevent parts of the synthetic
 resin from adhering to the surface of the

mould on removal of the moulded product.
 Substances conventionally used as mould-part-
 ing agents are e.g. waxes, soaps or oils. This
 mould-parting agent forms a thin film between
 the surface of the mould and the synthetic
 resin. This film adheres neither to the mould
 nor to the synthetic resin and thus facilitates
 removal of the product from the mould.

This method has various disadvantages in
 mass production. The mould-parting agent
 must be applied at regular intervals. During
 these periods, the mould is not available for
 production. Fine markings in the mould, e.g. to
 imitate the structure of wood or the grain
 of leather, become covered with residues of
 mould-parting agent in the course of time.
 Removal of these firmly adhering residues from
 the moulds which often have sharp contours
 is very difficult. Furthermore, the moulded
 products are covered with a thin film of
 mould-parting agent to which lacquer systems
 will not adhere. They must be ground, or
 cleaned with solvents, before they can be
 lacquered in order to ensure firm bonding of
 the lacquer to the synthetic resin.

It has now been found that the application
 of a mould-parting agent to the mould may
 be omitted if certain additives which impart
 excellent mould-parting properties to the
 finished synthetic resin product are added to
 the foamable reaction mixture.

Accordingly the present invention provides
 a process for the production of a foam resin
 by foaming, in a closed mould, a reaction
 mixture which comprises at least one polyiso-
 cyanate, at least one compound containing
 reactive hydrogen atoms, a blowing agent and
 a mould-parting agent, which mould-parting
 agent is a mixture of at least two of the fol-
 lowing components A, B and C:

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- 5 A. a salt of an aliphatic carboxylic acid and an amine, which salt contains at least 20 aliphatic carbon atoms,
 B. an ester of a monofunctional and/or polyfunctional carboxylic acid, which contains —COOH and/or —OH groups, and has an —OH or acid number of at least 5, and
 C. a natural or synthetic oil, fat or wax.

10 Since these mixtures also effect internal lubrication of the synthetic resin mixtures, they also impart excellent flow properties to the synthetic resin inside the mould and reduce the formation of bubbles on the surface of the synthetic resin. In addition, these additives have an antistatic effect.

15 The force in kg wt/cm² required to open the moulds on removal of the products may be taken as a measure of the mould-parting effect. Alternatively, the mould-parting effect may be assessed by measuring the force in kg wt required to strip an aluminium foil from a foamed polyurethane foam panel (20 × 20 × 1 cm). The mould-parting forces required for synthetic resins which contain mould parting agents according to the invention are considerably lower than those required for similar synthetic resins which have been produced by foaming a reaction mixture which does not contain the mould parting agents according to the invention and they are lower than those required when only one component of the ternary mixture has been used, i.e. there is an unexpected synergistic effect.

35 It should be noted that foaming in a closed mould produces a foam resin which has a higher density than one which has been foamed in an open mould. It also characteristically produces a firm, non-cellular, closed outer skin which is considerably thicker than the cell walls in the interior of the foam. This outer skin, which substantially determines the characteristic properties of the above described rigid, semi-rigid or soft polyurethane foam resin and its use properties, is thus not itself a foam resin. This is particularly conspicuous if, as is usually the case, the outer skin has a thickness of up to several millimeters.

50 A foam resin of this type, therefore, cannot be compared directly with conventional foam resins produced in open moulds, which normally do not have a continuous outer skin or otherwise only have a thin outer skin, the thickness of which is comparable to the thicknesses of the cell walls in the interior of the foam. The measures required to remove polyurethane foam resins which have been obtained by the process described above from their moulds therefore cannot be deduced from the formulations conventionally used for foam resins which are foamed in open moulds since it is precisely in the zone adjacent to the wall

of the mould that the material does not have the character of a foam resin.

Although conventional foam resin formulations have included fatty acids, sulphonic acids, tertiary fatty amines or certain surfactants to retard or promote the formation of the foam or as emulsifiers, no information has previously been given about the effect of these substances in promoting mould-parting agents in a foam resin which has a relatively thick, homogeneous external layer which does not have the structure of a foam, or else these substances have no such effect when producing the foam resins by the process described here or any effect that would be obtained is vitiated by other disadvantages.

Thus, the presence of sulphonic acids in the external layer of such foam resins reduces the resistance to weathering and foam formation may be adversely influenced, i.e. retarded. Tertiary amines tend to exude from the product, since they obviously cannot be chemically bound in the structure of the polyurethane and they impair lacquering of the covering layers. Products which have a pronounced surfactant character are also unsuitable since they promote degradation of the surface by hydrolytic influences.

According to the invention, these disadvantages are avoided if the mould-parting agents contain at least two of the components A, B and C. The components are as follows:

- A. Salts of aliphatic carboxylic acids with amines which salts contain at least 20 aliphatic carbon atoms. Preferably primary amines, or amines which contain amide groups or esters groups are used to form the salts. A satisfactory mould-parting effect is not achieved unless the salts have a total of at least 20 aliphatic carbon atoms distributed between the amine and acid. This means that the amine may be a short chained amine, if the carboxylic acid is a long chained acid, or the carboxylic acid may be a short chained acid if the amine has a long chain. It is preferable, however, if both the amine, either a primary amine or one which contains amides and/or ester groups, and the carboxylic acid each contain more than 12 aliphatic carbon atoms.
- B. Esters preferably of higher aliphatic or cycloaliphatic mono- and/or polyfunctional fatty acids or fatty acid mixtures with polyfunctional alcohols, the esters still containing free OH and/or COOH groups.
- C. Natural or synthetic oils and/or waxes need not contain any OH or COOH groups.

The mould parting agents may thus be

binary mixtures of A and B, or A and C, or B and C or ternary mixture of A, B and C.

It must be regarded as surprising that the use of these mixtures leads to valuable results without entailing disadvantages, e.g. with regard to lacquering of the surface. It was particularly surprising that the mixtures used according to the invention have a synergistic effect.

It must be regarded as surprising that these mixtures are effective although they contain (synergistically acting) components which in part carry groups which are capable of reacting with isocyanates, which would be expected to render them ineffective. Moreover, the quality of the foams is not impaired although the additives, insofar as they are monofunctional, would be expected to cause chain breaking. Another surprising feature is that the moulded products produced using the additives according to the invention show no deterioration in their ability to be lacquered. The mould parting agent mixtures according to the invention are preferably used in quantities of 0.1 to 25% by weight, more preferably 0.5 to 15% by weight, based on the total mixture.

The foamable reaction mixture is prepared from substances well known for this purpose, i.e. polyisocyanates, compounds which have at least two hydrogen atoms which are reactive with isocyanates and additives; a wide variety of these substances has been described in "Vieweg-Hochtlen, Kunststoffhandbuch, Volume VII, Polyurethane".

Polyisocyanates of any type may be used according to the invention. Diisocyanates are examples of especially advantageous polyisocyanates, e.g. tetramethylene diisocyanate, hexamethylene diisocyanate, m-xylylene diisocyanate, hexamethylene diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate, cyclohexane - 1,4 - diisocyanate, dicyclohexylmethane - 4,4' - diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 1-alkylbenzene - 2,4- and 2,6-diisocyanates, ditolylene - 2,4- and 2,6-diisocyanates, 3-(α -isocyanato-ethyl)-phenyl isocyanate, 1-benzylbenzene - 2,6-diisocyanate, 2,6-diethylbenzene - 1,4-diisocyanate, diphenylmethane - 4,4' - diisocyanate, 3,3'-dimethoxy-diphenylmethane-4,4' - diisocyanate and naphthylene - 1,5-diisocyanate. Trifunctional and higher functional polyisocyanates may also be used, e.g. toluene - 2,4,6-triisocyanate, polymethylene-polyphenyl - polyisocyanate obtained by aniline/formaldehyde condensation and subsequent phosgenation, the polyisocyanates which can be prepared according to German Patent Specification No. 1,092,007, and modified 4,4'-diphenylmethane diisocyanate liquefied by reaction with low molecular weight glycols such as tripropylene glycol.

Isocyanates which contain carbodiimide groups, uretdione groups, uretoneimine groups, biuret groups and isocyanurate groups may also be used as may also mixtures of the above mentioned isocyanates. Reaction products of polyhydric alcohols and polyfunctional isocyanates may be used, or the polyisocyanates used e.g. according to German Patent Specification Nos. 1,022,789 and 1,027,394.

Compounds which contain at least two hydrogen atoms reactive with isocyanates are understood to be preferably polyhydroxyl compounds or polyamines. These compounds have molecular weights of 90 to 10,000, preferably 90 to 5000.

Linear or branched polyesters or polyester amides which are prepared by known processes from monofunctional or polyfunctional alcohols and carboxylic acids or hydroxy carboxylic acids, if desired with the addition of amino-alcohols, diamines, hydroxylamines or amino-carboxylic acids and which may also contain hetero atoms, double and triple bonds and modifying radicals of unsaturated or saturated fatty acids or fatty alcohols are given as examples. Linear polyalkylene glycol ethers with various molecular weights obtained by the polymerisation of alkylene oxides, such as ethylene oxide, propylene oxide, styrene oxide, epichlorohydrin or tetrahydrofuran are also suitable, especially those which have a hydroxyl group content of 0.5 to 18%. Polyalkylene oxides which carry at the ends of the chains groups which have free primary or secondary amino groups are also suitable. The following are given as examples of polyfunctional starting materials for the addition reaction of the alkylene oxides:

H₂O, ethylene glycol, 1,2-propylene glycol, trimethylol propane, 1,2,4-butane triol, glycerol, pentaerythritol, sorbitol, oligosaccharides and their aqueous solutions, polysaccharides, castor oil, ethanalamine, diethanalamine, triethanalamine, aniline, arylene diamines, alkylene diamines such as ethylene diamine, tetra- or hexa-ethylene diamine and ammonia. Mixtures of various types of linear and/or branched polyalkylene glycol ethers may, of course, also be used. These polyalkylene glycoethers may also be used in admixture with other hydroxyl compounds or amines, e.g. with 1,4-butyleneglycol, trimethylol propane, glycerol, 2,3-butyleneglycol, pentaerythritol, tartaric acid esters, castor oil or tall oil.

Polyalkylene glycol ethers may be foamed also as mixture with polyesters. Other suitable reactants include:

OH-containing polycarbonates, polyacetals, polyamides, polyactones, polylactams, polytetrahydrofurans containing Cl and OH groups, and polybutadienes.

The following are also examples of suitable compounds which are reactive with isocyanates:

Polythioethers which have OH and/or SH groups, phenols reacted with alkylene oxide, formaldehyde resins, hydrogenation products of ethylene and carbon monoxide copolymers, epoxy resins, compounds containing amino groups, such as aminopolyethers, polyesters or polyurethanes, compounds which contain carboxyl groups and/or cyclic anhydride groups; the last mentioned compounds may in addition contain ether, ester, amide, urea, urethane or thioether groups.

The additives used according to the invention are binary or ternary mixtures. Component A are salts of aliphatic carboxylic acids with primary amines or with primary, secondary or tertiary amines which contain amide and/or ester groups; the salt should have a total of at least 20 aliphatic carbon atoms. Although it is preferred to use a mixture containing a stoichiometric proportion of acid and amine, deviations from the stoichiometric ratio of carboxyl groups to amino groups are acceptable although the excess of carboxyl groups or amino groups should not be more than 50 mols percent.

The carboxylic acids used for the formation of the salts may be monocarboxylic acids or polycarboxylic acids and they may be saturated or unsaturated and may also be substituted, but the preferred carboxylic acids are straight chain or branched long chain aliphatic monocarboxylic acids which contain more than 12 carbon atoms. The following are given as examples: stearic acid, commercial mixtures of fatty acids obtained from coconut oil, fatty acids obtained from tallow oil or train oil, commercial paraffin fatty acids which are usually mixtures, undecylenic acid, oleic acid, linoleic acid, tall oil fatty acids and ricinoleic acid. It is simplest to use oleic acid or tall oil.

The primary amines preferably used for formation of the salts may be straight chain, branched chain or cyclic and they may be monoamines, diamines or polyamines and have two or more carbon atoms. It is preferred to use aliphatic monoamines which contain more than 12 carbon atoms. The following are given as examples: stearylamine, oleylamine, amines obtained from ketones of commercial mixtures of long chain fatty acids, for example a 9-aminoheptadecane mixture, and tallow amines. So-called resinic amines obtained from resinic acids, or abietylamine, may also be used. A suitable diamine is ethylene diamine. The salts of 1 mol of oleic acid and 1 mol of oleylamine, 0.5 mol of ethylene diamine or 1 mol of 9-aminoheptadecane should be especially noted.

The amines which contain amide and/or ester groups may be primary or secondary amines but are preferably tertiary amines. They may easily be obtained e.g. by reacting diamines such as ethylene diamine, propylene diamine, N-dimethylamino propylamine or

polyamines with fatty acids under conditions which lead to amide formation, the quantity of fatty acid being chosen so that the amide formed still contains at least one free primary, secondary or, preferably, tertiary amino group. The fatty acids mainly used for this purpose are any aliphatic monocarboxylic or polycarboxylic acids, but the fatty acids used are preferably saturated or unsaturated monocarboxylic acids containing more than 12 carbon atoms, for example the types already mentioned above.

The amide-containing amine obtained from N - dimethyl - aminopropylamine and oleic acid should be especially noted because it is so easily obtainable by commercial processes.

Basically, the same considerations apply to the amines containing ester groups, which are preferably tertiary amines. They may also be obtained in known manner, for example by reacting the addition product of alkylene oxides to primary or secondary amines or polyamines, for example alkanolamines such as triethanolamine, N-dimethyl ethanolamine, N-dioleylethanolamine or ethylene diamine, with the above mentioned fatty acids under conditions which lead to esterification. The amine obtained from 3 mols of maleic acid and 1 mol of triethanolamine or from tall oil fatty acid and propoxylated ethylene diamine should be especially noted.

Component A of the mould parting mixture is most easily prepared by simply mixing the carboxylic acid with the amine, if desired in the melt or in solution. One variation of this method consists of mixing the components in one or more of the constituents of the foaming mixture.

Component B of the additive mixture consists of saturated and/or unsaturated esters of monofunctional and/or polyfunctional carboxylic acids with alcohols which are preferably polyfunctional, the said esters containing COOH and/or OH groups.

The polyfunctional carboxylic acids should preferably contain at least four carbon atoms, for example maleic acid, succinic acid, glutaric acid, adipic acid, suberic acid, sebacic acid or heptadecane-1,8-dicarboxylic acid or oligomeric or polymeric compounds which contain carboxyl groups, e.g. oxidised polyethylene.

The monofunctional carboxylic acids may be saturated or unsaturated and may also contain other polar or non-polar groups, e.g. OH, amino, alkyl, halogen or aryl groups. It is preferred to use aliphatic carboxylic acids, either branched or straight chain, which contain more than 12 carbon atoms. The following are given as examples: stearic acid, palmitic acid, ricinoleic acid, commercial fatty acid mixtures such as those obtained from coconut oil, fatty acids from tallow oil or from fish oil, resinic acids, e.g. abietic acid, tall oil fatty acids, linoleic acid, linolenic acid, undecylenic

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acid and commercial paraffin fatty acids; oleic acid and tall oil fatty acid are very suitable.

The esters are advantageously prepared from monocarboxylic acids, if desired mixed with polyfunctional carboxylic acids.

The alcohol component of the ester used as component B preferably consists of polyfunctional alcohols which are preferably aliphatic in character, for example ethylene glycol, propylene glycol, butylene glycol, polyalkylene glycols, hexane diol, glycerol, trimethylol propane, pentaerythritol, sorbitol, hexitol, glucose, sucrose or addition products of one or more alkylene oxides to these alcohols or to amines, such as adducts of alkylene oxides such as ethylene oxide or propylene oxide with glycerol, trimethylol propane or ethylene diamine. In the case of ricinoleic acid, for example, the desired ester can be produced by internal condensation without the addition of an alcohol.

The esters are usually prepared by known methods, either with or without the addition of an acid or basic catalyst, metal alcoholate or similar known auxiliary agent, at elevated temperature and preferably with exclusion of air.

The esters used may also have the character of polyesters with molecular weights of up to 5000.

The esters should contain OH and/or COOH groups, i.e. they should have an acid number or OH number of at least 5, and preferably more than 10.

Especially suitable esters are esterification products of glycerol, trimethylol propane, pentaerythritol, sorbitol or sugars with oleic acid or tall oil fatty acid, in which on average at least one OH group is not esterified.

Mixtures of various such esters may, of course, also be used.

Component C is natural and/or synthetic oils or waxes. These components need not contain free COOH or OH groups. They may be ester derivatives or carboxylic acid derivatives, e.g. those which frequently occur in natural oils and waxes or which can be obtained on complete esterification of polyols.

The following list of substances which may be used either singly or as mixtures is given by way of example and is not exhaustive: lanolin, beeswax, mineral waxes, plant oils, bone oil, sesame oil, wool fats, white oil, petroleum fractions having boiling points above 100° C, paraffin oil, Vaseline (Registered Trade Mark), abietic acid esters, cholesterol esters and train oils. White oil and lanolin are especially suitable.

In the binary or ternary mould parting mixture, each of the components should preferably be present in an amount of at least 5% by weight, and more preferably at least 15% by weight. The ternary mixture should preferably contain 20 to 50% by weight of each component and the binary mixture 20 to 80%,

with the percentages, of course, adding up to 100%.

The mould parting agent need not necessarily be added as such. Individual components of the mixture may be added singly or in combinations of two either to the whole foaming mixture or dissolved in different constituents of the foaming mixture, but when the foaming mixture is already undergoing reaction, it should contain all the components of the mould parting agent mixture of the process.

The mixtures used according to the invention and preferably used in quantities of 0.1 to 25% by weight, more preferably 0.5 to 15% by weight, based on the whole foaming mixture.

It is preferred to use mould parting agent mixtures which are liquid at room temperature and/or which can be dissolved, if desired, in the form of solutions of the individual components in one or more components of the foaming mixture.

Apart from fillers, dyes, etc., there may be used flame-retarding additives. These flame-retarding additives may be substances containing groups which are reactive with isocyanates, e.g. reaction products of phosphoric acid or phosphorus acid or phosphonic acids and alkylene oxides, or alkylene glycols or reaction products of dialkyl phosphites, formaldehyde and dialkanolamines. Alternatively, they may be substances which are free from groups that are reactive with isocyanates, e.g. tris-2-chloroethyl phosphate, tricresyl phosphate or tris-dibromopropyl phosphate.

The usual activators may be used for the production of the foam resins, e.g. dimethylbenzylamine, N-methyl-N-(N,N-dimethylaminoethyl)-piperazine, triethylene diamine, permethylated diethylene diamine, tetramethyl guanidine, trihydroxymethyl hexahydrotriazine or organic tin compounds such as dibutyl tin dilaurate or tin(II) octoate. Stabilisers such as polyethers, polysiloxanes or sulphonated derivatives of castor oil or of oleic acid and their sodium salts can also be used.

Water and/or low boiling solvents such as trichloromonofluoromethane, dichlorofluoromethane and methylene chloride are used as blowing agents. These blowing agents are generally used in quantities of 10 to 15 parts by weight, based on 100 parts by weight of the compound which contains groups reactive with isocyanates.

Preparation of the products may be adjusted to produce rigid products used for the manufacture of parts of furniture, parts of automobile bodies, technical apparatus and structural elements or semi-rigid to soft products for the manufacture of safety cushions used in the construction of automobiles or the manufacture of elastic shoe soles.

The process of the invention will now be

explained with the aid of examples. The parts given are parts by weight unless otherwise indicated.

Example 1.

- 5 Using two different foaming mixtures and several typical components A, B and C it will be demonstrated that the use of individual components is not sufficient to provide completely satisfactory removal of a rigid moulded foam resin product produced in a metal mould, but that co-operation of two or three components results in very satisfactory mould parting.

Foaming mixture A:

- 15 100 parts of polyether polyol mixture, activated and stabilised (OH number: 530, viscosity at 25° C: 1250 cP),*
4 part of monofluorotrichloromethane,
20 150 parts of polyisocyanate (based on phosgenation of aniline/formaldehyde condensates) (viscosity at 25° C: 320 cP; NCO content: 29.5%).

Foaming mixture B:

- 25 100 parts of polyether polyol mixture activated and stabilised (OH number: 490, viscosity at 25° C: 1429 cP),*
4 parts of monofluorotrichloromethane.
132 parts of polyisocyanate according to A.

- 30 The polyol mixture and blowing agent are introduced into a two-component dosing and mixing apparatus, optionally in admixture with the mould parting agent, and in this apparatus they are vigorously mixed with the given quantity of polyisocyanate to produce the foamable reaction mixture and the mixture is immediately forced under pressure into the metal mould which is at a temperature of 60° C.

- 40 The mould, which is a rectangular box having a wall thickness of 15 mm, has the following dimensions: Base: 360 × 250 mm, height of side wall: 40 mm. Shearing forces must be overcome in order to remove the product from the mould. The synthetic resin product is removed from the mould after 6 minutes. The mould is attached to a hydraulic closing unit which enables the opening forces to be accurately measured.

- 50 A force detecting element converts the opening force into an electric signal which is amplified in a carrier frequency amplifier and recorded with a compensating continuous line recording instrument. The specific opening forces are calculated from the recorded data.

- 55 Below are given examples of components A, B and C used:

Component D:

Stoichiometric tall oil fatty acid salt of 1

* Described in more detail below.

mol of tall oil fatty acid and 1 mol of an amidoamine, prepared from 1 mol of N,N-dimethyl - aminopropylamine - 1 and 1 mol of tall oil fatty acid. Oleic acid may be used instead of tall oil fatty acid.

Component E:

Salt of 1 mol of oleic acid and 1 mol of dihydroabietylamine (resinic amine of Hercules Powder, Inc.).

Component H:

Ester of 1 mol of pentaerythritol and about 3 mols of oleic acid (OH number approximately 90).

Component I:

Ester of about 4 mols of train oil fatty acid and 1 mol of sorbitol (OH number approximately 130).

Component K:

Ester of 1 mol of adipic acid, 2 mols of sorbitol and about 9 mols of tall oil fatty acid (acid number approximately 9, OH number approximately 15).

Component O:

Commercial white oil.

Component P:

Commercial lanolin.

Component Q:

Commercial sesame oil.

Components D and E are salts as defined in component A.

Components H, I and K are esters as defined in component B. Components O, P and Q are natural or synthetic oils, fats or waxes as defined in Component C.

The following experiments demonstrate that each of the three components requires higher mould-parting forces when used on its own.

Comparison Example 1.

8 Parts of component D are added to foaming mixture A. The resulting moulded foam product can be removed from the mould only with a hydraulic power of more than about 300 kg wt and the power levers tear open the mould with a force of about 6 kg wt/cm².

Comparison Example 2.

8 Parts of component I are added to foaming mixture A. The resulting foam product can be removed from the mould only with a hydraulic power of more than 300 kg wt. The power levers tear open the mould with a force of 7 kg wt/cm².

Comparison Example 3.

8 Parts of component O are added to foaming mixture A. The resulting moulded foam product can be removed from the mould only

with a hydraulic power of more than 300 kg wt. The power levers tear open the mould with a force of about 8 kg wt/cm².

5 These examples show that the individual components of the mould parting mixture do not have the desired result of enabling the moulded product to be easily removed from the mould.

Analogous results are obtained by using foaming mixture B instead of foaming mixture A in Examples 1 to 3.

The following Table which describes the use of the ternary mixtures according to the invention shows that mould parting is distinctly improved thereby.

TABLE I

Example No.:	1a	1b	1c	1d	1e	1f	1g
Foaming mixture A, parts	254	254	254				254
Foaming mixture B, parts				236	236	236	
Component D, parts	6	3	3	2.5		1.5	3
Component E, parts					5	1.5	
Component H, parts					3		2
Component J, parts	1.8	1.8	1.8	2.5			
Component K, parts						3	2
Component O, parts	1.2	1.2	1.2	3			1
Component P, parts		2			2	3	1
Component Q, parts			2				1
Hydraulic power, kg wt	126	98	135	125	105	120	115
Specific opening force, kt wt/cm ²	1.0	0.78	1.1	0.9	1.5	1.3	1.0

Example 2.

Using two different foaming mixtures which use several typical components A, B and C it will now be demonstrated that the individual components are not sufficient on their own to result in completely satisfactory removal of a semi-rigid to soft moulded foam resin product produced in a metal mould but that co-operation of all three components results in very satisfactory mould parting.

Foaming mixture A:

- 100 parts of polyether polyol mixture, activated, stabilised (OH number: 180, viscosity at 25° C: 1000±100 cP),*
- 8 parts of monofluorotrichloromethane,
- 4 parts of methylene dichloride,
- 48 parts of polyisocyanate (based on phosgenation of aniline/formaldehyde condensation) (viscosity at 25° C: <100 cP, NCO content: 30±1%).

Foaming mixture B:

- 100 parts of polyether polyol mixture, activated, stabilised (OH number: 150, viscosity: 600±100 cP/25° C),*
- 6 parts of monofluorotrichloromethane,
- 52 parts of polyisocyanate (based on phosgenation of aniline/formaldehyde condensation) (viscosity: 700 cP/25° C; NCO content: 23±1%).

The polyol mixture and blowing agent are introduced into a two-component dosing and mixing apparatus, optionally together with the mould parting mixture, and in this apparatus they are vigorously mixed with the given quantity of polyisocyanate to produce the foamable reaction mixture which is then immediately forced into the metal mould which is at a temperature of 60° C.

The moulding tools were original automobile arm rest moulds made of pressure die cast zinc. In order to effect removal from the mould, shearing forces must be overcome. The synthetic resin product is removed from the mould after 5 minutes. To determine the forces required to open the mould, an aluminium strip is removed at a specified rate from a foamed sample plate (20 × 20 × 1 cm) and the force required for this is measured.

* Described in more detail below.

Dimensions of sample:

Total length of sample	150 mm	50
width of sample	50 mm	
length of foil removed	18 mm	
thickness of foam layer	10 mm	
thickness of aluminium foil	0.2 to 0.3 mm	55
Rate of removal of stripping	50 mm/min.	

Components D, I and O are used as examples in the same way as described in Example 1.

The following experiments show that also in the semi-rigid to soft polyurethane systems each of the three components of the ternary additive mixture used on its own requires larger separating forces.

Comparison Example 4.

3 Parts of component O are added to foaming mixture A. The force with which the aluminium foil is bonded to the foam resin plate is 610 pond. When 3 parts of component O are added to foaming mixture B, the force with which the aluminium foil is bonded to the foam resin plate is 2650 pond.

Comparison Example 5.

3 Parts of component I are added to foaming mixture A. The force with which the aluminium foil is bonded to the foam resin plate is 400 pond. When foaming mixture B is used instead of foaming mixture A, the strength of the bond is 1100 pond.

Comparison Example 6.

3 Parts of component D are added to foaming mixture A. The force with which the aluminium foil is bonded to the foam resin plate is 350 pond. When foaming mixture B is used instead of foaming mixture A, the bonding force is 1060 pond.

These examples show that the individual components do not allow the resulting moulded product to be easily removed from the mould as is desired.

The following table which describes the use of the ternary mixture in accordance with the invention shows that mould parting is distinctly improved by the synergistic mixtures according to the invention.

TABLE II

Example No.:	2a	2b	2c	2d	2e	2f	2g	2h
Foaming mixture A, parts	160	160	160	160				
Foaming mixture B, parts					158	158	158	158
Component D, parts	3			1	3			1
Component I, parts		3		1		3		1
Component O, parts			3	1			3	1
Bonding of an aluminium foil to the foam resin product, pond.	305	400	610	240	1060	1100	2650	990

The mould-parting values may, of course, be further improved by increasing the quantity of ternary additive mixture but the examples given are intended to show the effectiveness of comparatively small quantities of additive.

Example 3.

Using two different foaming mixtures which use several typical components A and C of a binary synergistic additive mixture according to the invention, it will now be demonstrated that the individual components of the binary mixture are not sufficient on their own to result in completely satisfactory removal from the mould of a rigid foam resin product produced in a metal mould but that co-operation of the two components results in very satisfactory mould parting.

Foaming mixture A:

100 parts of polyol mixture (based on polyether), activated and stabilised (OH number: 530, viscosity at 25° C: 1250 cP),
4 parts of monofluorotrichloromethane.
150 parts of polyisocyanate (based on phosphorylation of aniline/formaldehyde condensates) (viscosity at 25° C: 320 cP, NCO content: 29.5%).

Foaming mixture B:

100 parts of polyol mixture (based on polyether), activated and stabilised (OH number: 490, viscosity at 25° C: 1420 cP),
4 parts of monofluorotrichloromethane.
132 parts of polyisocyanate according to A.

The polyol mixture and blowing agent are introduced into a two-component dosing and mixing apparatus, optionally in admixture with the additive which facilitates mould parting, and in this apparatus they are vigorously mixed with the given quantity of polyisocyanate to produce the foamable reaction mixture which is then immediately forced into a metal mould which is at a temperature of 60° C, as already described fully in Example 1.

The time until removal from the mould is 6 minutes. The forces required for removal of the product from the mould are measured with the same system of measuring instruments as in Example 1.

The following components of the binary synergistic additive are used as examples:

Component D:

(See Example 1).

Component E:

(See Example 1).

Component F:

30 kg (106 mol) of oleic acid are mixed with 25.5 kg (100 mol) of 9-aminoheptadecane (C 15 to C 19 mixture) with stirring and mild cooling. The temperature rises to 40° C. The temperature has returned to room temperature after one hour and the product is then ready for use. Viscosity: η 25 = 77 cP.

Components O, P and Q:

(See Example 1).

Component R:

Commercial sorbitol hexaoleate (OH number approximately 21).

Components D, E and F thus are salts (as defined in component A. Components O, P, Q and R are natural or synthetic oils, fats or waxes as defined for Component 1.

Comparison Examples 1, 2, 3 and 7 demonstrate that none of the components of the binary additive mixture can provide an adequate mould-parting effect when used on its own.

Comparison Example 7.

8 Parts of component F are added to foaming mixture B. The resulting foam resin product can be removed from the mould only with a hydraulic power of more than 300 kg wt. The power levers open the mould with a force of about 6 kg wt/cm².

These examples show that the individual components of the binary mould-parting mixture on their own do not cause the resulting moulded products to be easily removed from the mould as desired.

Analogous results are obtained when using foaming mixture B instead of foaming mixture A in Comparison Examples 1, 2, 3 and 7.

The following table, which describes the effective use of the binary mixture, shows that mould parting is distinctly improved by the discovered synergistic effect.

TABLE III

Example No.:	3a	3b	3c	3d	3e	3f	3g
Foaming mixture A, parts	254	254	254				
Foaming mixture B, parts				236	236	236	236
Component D, parts	6	6	6			2	1
Component E, parts					6	1	1
Component F, parts				5			1
Component O, parts			3		1	2	
Component P, parts	3			4		2	
Component Q, parts		3					2
Component R, parts					2	1	2
Hydraulic power, kg wt	91	150	170	160	165	170	160
Specific opening force, kg wt/cm ²	0.72	1.2	1.5	1.3	1.4	1.3	1.2

The mould-parting values may, of course, be further improved by increasing the quantity of ternary additive mixture, but the examples given are intended to show the effectiveness of comparatively small quantities of additive.

Example 2. The strength of the bond of the material to the metal is measured with the aid of the stripping forces required for stripping an aluminium foil from the foam resin product as described in detail in Example 2.

Example 4. The values are summarised in Table IV. It can be easily seen that the mould parting is improved by the discovered synergistic effect.

TABLE IV

Example No.:	4a	4b	4c	4d	4e	4f
Foaming mixture A, parts	160	160	160			
Foaming mixture B, parts				158	158	158
Component D, parts	3		1.5	3		1.5
Component O, parts		3	1.5		3	1.5
Force with which an aluminium foil is bonded to the foam resin product, pond.	305	610	150	1060	2650	570

Once again the mould-parting values could be further improved by increasing the quantity of binary additive mixture used.

Example 5.

- 5 Using two different foaming mixtures which use several typical components B and C according to the invention, it will now be demonstrated that the individual components of the binary mixture when used on their own are not capable of providing completely satisfactory mould parting of a moulded foam resin product produced in the metal mould but that co-operation of the two components results in very satisfactory mould parting.

15 Foaming Mixture A:

- 100 parts of polyol mixture (based on poly-ether), activated and stabilised (OH number: 530, viscosity at 25° C: 1250 cP),
 20 4 parts of monofluorotrichloromethane,
 150 parts of polyisocyanate (based on phos-genation of aniline/formaldehyde condensates viscosity at 25° C: 320 cP, NCO content: 29.5%).

25 Foaming mixture B:

- 100 parts of polyol mixture (based on poly-ether), activated and stabilised (OH number: 490, viscosity at 25° C: 1420 cP),
 30 4 parts of monofluorotrichloromethane,
 132 parts of polyisocyanate according to A.

- The polyol mixture and blowing agent are introduced into a two-component dosing and mixing apparatus, optionally together with the additive which facilitates mould parting, and in this apparatus they are vigorously mixed with the given quantity of polyisocyanate to produce the foamable reaction mixture which is then immediately forced into the hot metal mould which is at 60° C, as described in detail in Example 1.

- The mould parting time is 6 minutes. The forces required for mould parting are measured with the same system of measuring instruments as in Example 1.

The following additional components of the binary synergistic additive mixture is used:

Component G:

Ester of 5 mols of train oil fatty acid and 1 mol of sorbitol (OH number approximately 55).

Components O, P and Q:

As described in Example 1.

Component G is an ester containing component as defined in component B.

Components O, P and Q are "natural or synthetic oils, fats or waxes".

The following experiments show that none of the components of the binary additive mixture can produce a sufficient mould parting effect when used on its own.

Comparison Example B.

8 Parts of component G are added to foaming mixture A. The resulting moulded foam resin product can be removed from the mould only with a hydraulic power of more than about 300 kg wt and the power levers tear open the mould with a force of about 6.6 kg wt/cm².

Comparison Example 8.

8 Parts of Component O are added to foaming mixture A. The resulting moulded foam resin products can be removed from the mould only with a hydraulic power of more than 300 kg wt. The power levers tear open the mould with a force of about 8 kg wt/cm².

These examples show that the individual components of the binary mould-parting mixture used on their own do not cause the resulting moulded product to be easily removed from the mould as desired.

Analogous results are obtained when using foaming mixture B instead of foaming mixture A in Comparison Examples 8 and 9.

The following table, which describes the effective use of the binary mixture, shows that mould parting is distinctly improved by the synergistic mixtures according to the invention.

TABLE V

Example No.:	5a	5b	5c	5d	5e	5f
Foaming mixture A, parts	254	254	254			254
Foaming mixture B, parts				236	236	
Component D, parts	3				2	
Component E, parts		3				
Component F, parts			3		3	
Component G, parts				4		5
Component O, parts	3			1	4	
Component P, parts		3		3		
Component R, parts			3			5
Hydraulic power, kg wt	137	160	130	128	125	133
Specific opening force, kg wt/cm ²	1.1	1.3	1.0	1.1	1.0	1.2

The mould-parting values may, of course, be further improved by increasing the quantity of binary additive mixture, but the examples given are intended to show the effectiveness of comparatively small quantities of additive.

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Example 6.

A synergist binary additive mixture is studied in foaming mixtures A and B, as in Example 2. The strength

with which the material adheres to the metal is measured with the aid of the stripping forces required for stripping an aluminium foil from the foam resin product, as already described in detail in Example 2.

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The values are summarised in Table VI. They show clearly that mould parting is distinctly improved by the discovered synergistic mixtures according to the invention.

TABLE VI

Example No.	6a	6b	6c	6d	6e	6f
Foaming mixture A, parts	160	160	160	160		
Foaming mixture B, parts					158	158
Component I, parts	3			1.5	3	1.5
Component O, parts			3	1.5		1.5
Strength of adherence of an aluminium foil to the foam resin product, pond.	890		610	580	2400	2650
						1500

20 Here again the mould-parting values may be improved by increasing the quantity of binary additive mixture.

The polyol mixtures used in Example 1 and 2 were as follows: —

25 Polyol mixture of Example 1 A (OH number 530):
60 parts by weight of propoxylated trimethylolpropane (OH number 830)

40 parts by weight of a polyether having an OH number of 42 made by adding a mixture of propylene oxide and ethylene oxide to a mixture of trimethylolpropane and 1,2-propane diol (molar ratio of the starters 1:3).

1 part by weight of a polysiloxane-based stabilizer.

3 parts by weight of dimethylbenzylamine.
0.6 parts by weight of tetramethylguanidine.

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- Polyol mixture of example 1 B (OH number 490):
- 60 parts by weight of propoxylated ethylene diamine (OH number 650).
 - 20 parts by weight of propoxylated trimethylol propane (OH number 330).
 - 20 parts by weight of a polyether having an OH number of 28 obtained by adding a mixture of ethylene oxide and propylene oxide to 1,2-propane diol.
 - 1 part by weight of a polysiloxane-based stabilizer.
 - 0.1 part by weight of 1-methyl-4-(N,N-dimethyl-aminoethyl)-piperazine.
- Polyol mixture of example 2 A (OH number 180):
- 88 parts by weight of a polyether having an OH number of 35 obtained by adding a mixture of propylene oxide and ethylene oxide to trimethylolpropane.
 - 12 parts by weight of 1,4-butane diol.
 - 0.5 parts by weight of diazabicyclooctane.
- Polyol mixture of example 2 B (OH number 150):
- 91 parts by weight of a linear polyether having an OH number of 48 obtained by adding a mixture of ethylene oxide and propylene oxide to 1,2 propylene glycol.
 - 9 parts by weight of 1,4-butane diol.
 - 0.4 parts by weight of diazabicyclooctane.
 - 0.02 parts by weight of dibutyl-tin-dilaurate.
- WHAT WE CLAIM IS:—
1. A process for the production of a foam resin by foaming, in a closed mould, a reaction mixture which comprises at least one polyisocyanate, at least one compound containing reactive hydrogen atoms, a blowing agent and a mould-parting agent, which mould-parting agent is a mixture of at least two of the following components A, B, and C:
 - A. a salt of an aliphatic carboxylic acid and an amine, which salt contains at least 20 aliphatic carbon atoms,
 - B. an ester of a monofunctional and/or polyfunctional carboxylic acid, which contains —COOH and/or—OH groups, and has an —OH or acid number of at least 5, and
 - C. a natural or synthetic oil, fat or wax.
 2. A process as claimed in claim 1 in which a mixture of more than one salt, ester and/or oil, fat or wax is present in any of the components A, B and/or C.
 3. A process as claimed in claim 1 or claim 2 in which the salt A contains amide and/or ester groups.
 4. A process as claimed in any of claims 1 to 3 in which the blowing agent used is, or comprises, water.
 5. A process as claimed in any of claims 1 to 4 in which the mould-parting agent is a mixture of A and C.
 6. A process as claimed in any of claims 1 to 4 in which the mould-parting agent is a mixture of A and B.
 7. A process as claimed in any of claims 1 to 4 in which the mould-parting agent is a mixture of B and C.
 8. A process as claimed in any of claims 1 to 4 in which the mould-parting agent is a mixture of A, B and C.
 9. A process as claimed in any of claims 1 to 6 or 8 in which A is an oleic acid salt or tall oil fatty acid salt of an amido-amine which is obtained by reacting N-dimethylaminopropylamine with oleic acid or tall oil fatty acid.
 10. A process as claimed in any of claims 1 to 4 or 6 to 9 in which B is an oleic acid ester, a tall oil fatty acid ester, and/or a train oil fatty acid ester of a polyhydric aliphatic alcohol in which on average at least one OH group is not esterified.
 11. A process as claimed in any of claims 1 to 5 or 7 to 10 in which C is white oil, lanoline and/or paraffin oil.
 12. A process as claimed in any of claims 1 to 11 in which 0.1 to 25% by weight of mould-parting agent is used, based on the total weight of the foamable mixture.
 13. A process as claimed in claim 12 in which 0.5 to 15% by weight of mould-parting agent is used.
 14. A process as claimed in any of claims 8 to 13 in which each component of the mould-parting agent is present in an amount of at least 5% by weight, based on the weight of the mould-parting agent.
 15. A process as claimed in claim 14 in which each component is present in an amount of at least 15% by weight.
 16. A process as claimed in any of claims 1 to 7 or 9 to 13 in which each component of the mould-parting agent is present in an amount of 20 to 80% by weight in binary mixtures and 20 to 50% by weight in ternary mixtures based on the weight of the mould-parting agent.
 17. A process as claimed in claim 1 substantially as herein described with reference to any one of the Example.
 18. A foam resin when produced by a process as claimed in any of claims 1 to 17.

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